STANDARD OPERATING PROCEDURE

TITLE: Total Organic Carbon Analysis

DEPARTMENT: Inorganic - Wet Chemistry

APPLICATION: Determination of nonpurgeable carbon in water matrices. (TOC as NPOC).

REFERENCE: EPA 600 4-79-020, Revised March 1983, Method 415.1
EPA Manual SW-846, 3rd Edition, Method 9060
Dohrmann DC-190 High Temperature TOC Analyzer Operation Manual, Sept. 1994, Revision C

PROCEDURE SUMMARY:

The DC-190 system features a vertical quartz combustion tube packed with supported platinum catalyst which receives a continuous flow of oxygen or air at 200 cc/minute. The furnace is normally maintained at 680 °C but can be varied to any temperature up to 900 °C. Organic containing samples are manually or automatically introduced into the combustion tube via an air-actuated injection port. Through catalytic oxidation, the sample is completely oxidized to CO_2 and H_2O. The gas flow sweeps the CO_2 containing steam out of the combustion tube and into the IC reactor. It continues through a condenser, a gas liquid separator, and moisture trap. Final H_2O removal is accomplished by a permeation dryer. The dried CO_2 containing gas is then passed through a halogen scrubber and to a CO_2 specific non-dispersive infrared detector (NDIR) for peak quantification. Inorganic carbon (IC) samples are manually or automatically introduced into the IC reactor, which contains acidic water solution at room temperature, via an air-operated injection port. In this acidic environment, all forms of IC are purged out of the solution as CO_2 by the continuous flow of gas. The gas then continues through the drying system to the NDIR detector for quantitation.

LABORATORY DETECTION AND REPORTING LIMITS:

	LOD	EQL
Water:	0.33	1.0 mg/L

Approximate working range of method: LOD to 250 ppm.

REVIEWED BY: Jeffrey A. Gordon — Date: 4-19-99
Inorganic Section Supervisor

Gregory J. Graf — Date: 4-21-99
Quality Assurance Officer

APPROVED BY: Glen A. Coder — Date: 4-21-99
Glen A. Coder
Laboratory Manager

SAMPLE HANDLING & PRESERVATION:

A 125-mL sample is preserved in a glass(preferable) or plastic container at the time of collection by acidifying to pH $\leq$ 2 with sulfuric acid (H_2SO_4) or hydrochloric acid (HCL). The sample is then refrigerated to 4°C. Holding time for the preserved sample is 28 days from date of collection.

APPARATUS:

Dohrmann DC 190 Total Organic Carbon Analyzer
Autosampler Vials (10 mL volume)
Pipettors (0.1-100 µL, 100-1000 µL, 0.1-5.0 mL)
Syringes (50 µL, 100 - 250 µL, 1 mL)
Volumetric flasks (50 mL, 100 mL, 200 mL, 1000 mL)
Analytical balance
Top loader balance

REAGENTS:

Milli-Q deionized water
Nitric acid (HNO_3), concentrated
Potassium hydrogen phthalate (KHP), 2 sources
Oxygen gas, 99.9% purity grade
Phosphoric acid

Prepare stock standard, 2000 ppm as carbon, as follows:

- Dissolve 425 mg KHP in 100 mL Milli-Q water. Store in an amber bottle. Shelf life of one month.

Prepare calibration standard

- 5 ppm as follows: 0.25 mL of 2000 ppm to 100 mL of Milli-Q water
- 50 ppm as follows: 1.25 mL of 2000 ppm to 50 mL of Milli-Q water
- 250 ppm as follows: 6.25 mL of 2000 ppm to 50 mL of Milli-Q water

NOTE: The Linear range is not more than +10% of highest standard
All calibration standards listed above have a one week shelf life

PROCEDURE:

1. Start-up the instrument, specific for each matrix - soil or aqueous. (See EN CHEM SOP, WCM-18.)

2. To calibrate for TOC as NPOC, set up vials as follows:
   a. Vial #1, standard solution, no peg
   b. Vial #2, standard solution, peg on the outside
   c. Vial #3, Milli-Q water, no peg
   d. Vial #4, Milli-Q water, peg on the inside

3. Analyze 5.0, 50.0, and 250.0 mg/L standards from the same source as the calibration standard. The recovery must be ± 10%. If any recovery fails, recalibrate the instrument.

   a. Analyze an ICV sample(10 mg/L). Value must be ± 10%.
   b. Analyze an ICB sample. Value must be less than EQL.
   c. Analyze LCS sample. Value must be within current control limits .
   d. Analyze method blank (Milli-Q H_2O) sample. Value must be less than EQL.

4. Prepare samples as follows:

   a. Shake sample vigorously to suspend sediment.
   b. Pour into a clean vial for autosampler.
   c. Each sample will be composed of 3 injections. The first result in the triplicate may be omitted as this injection is used to prime the combustion tube. The average of the replicates is used for reporting.

   If referencing SW846 9060, Quadruplicate analysis is required for all samples. Each sample will be composed of 4 individual injections. Report all four individual injection readings and the average of the four readings. If the client desires to have SW846 9060 cited, but does not want Quadruplicate analyses performed, the default procedure for analysis will be followed and the method citation will be changed to SW846 9060Mod.

   For Quad analysis: The ICV, CCV, ICB, CCB, LCS and MB do not need to be read in quadruplicate, but the MS/MSD does need to be.

5. MS are prepared at 10 ppm by adding 0.025 ml of the 2000ppm stock standard to 4.975ml of sample (5.0 ml final volume).

6. The calibration established will be valid for several trays of samples up to a total of 20 samples. A new laboratory control sample (LCS) and method blank (MB), as well as additional matrix spike (MS) and matrix spike duplicate (MSD) must be added to continue samples analysis past 20.

7. Shut down instrument. (See EN CHEM SOP, WCM-18.)

QUALITY CONTROL:

- Calibration Check Standard
  Three standards are analyzed immediately after calibration to verify linearity. All must be from the same source as the calibration standard and meet the control limit of ± 10% of the true value.

- Replicates
  Replicates should meet a %RSD of 20 (unless the sample concentrations are < 5x the EQL). If not, repeat analysis, dilute sample and repeat, etc. until criteria is met.

- Initial Calibration Verification (ICV)
  The ICV must be run immediately after the three calibration check standards. It must be from a second source and meet current control limits of ± 10% of the true value. If not, recalibrate.

- Initial Calibration Blank (ICB)
  The ICB must be analyzed after the ICV and be less than the absolute difference of the estimated quantitation limit (EQL).

- Method Blank (MB)
  The MB is carried through all prep procedures and analyzed with a frequency of 5%. Rejection criteria is < LOD. Other criteria may apply, such as regulatory limit and analyte concentration in samples.

- Laboratory Control Sample (LCS)
  An LCS consisting of known concentration must be prepared and analyzed for each batch of 20 samples, and meet the current control limit.

- Continuing Calibration Verification (CCV)
  The CCV is analyzed after every 10 analytical samples and must meet current control limits of ± 10% of true value. If not, the calibration procedure must be repeated.

- Continuing Calibration Blank (CCB)
  The CCB is analyzed after every CCV and must be less than the absolute value of the EQL. If not, the calibration procedure must be repeated.

- Matrix Spike
  A spike must be performed on each group of samples of a similar matrix type with a frequency of 5%. Recovery must meet the current control limits.

- Matrix Spike Duplicate
  A matrix spike duplicate must be analyzed on each group of samples of a similar matrix type with a frequency of 5%. Recovery must meet the current control limits for accuracy and the difference between the MS and MSD must meet current control limits for precision.

CALCULATION:

The instrument provides calculated sample results in mg/L, calculations are only necessary if a dilution was used.

Raw Data Value (mg/L) x Dilution Factor = TOC as NPOC (mg/L)

ACCURACY:

A matrix spike and matrix spike duplicate must be performed on each group of samples of a similar matrix type with a frequency of 5% and meet the current control limits for accuracy. If method SW846 9060 is referenced, accuracy is to be at a frequency of 10%.

Spike calculation:

$$\% \text{ Recovery} = \frac{SSR-SR}{SA}$$

SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

If there is insufficient volume available for an MS/MSD, perform an LCS/LCSDUP

PRECISION:

A matrix spike duplicate must be analyzed on each group of samples of a similar matrix type with a frequency of 5% and meet the current control limits for precision. If method SW846 9060 is referenced, precision is to be at a frequency of 10%.

Use relative percent difference (RPD) calculation:

$$RPD = \frac{|MS-MSD|}{(MS+MSD)/2} \times 100$$

MS = Matrix Spike Value
MSD = Matrix Spike Duplicate Value

If there is insufficient volume available for an MS/MSD, perform an LCS/LCSDUP